UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH SERVICE
SOUTHERN UTILIZATION RESEARCH BRANCH

MEETING

of

THE TUNG INDUSTRY INFORMAL RESEARCH COMMITTEE

AT THE

SOUTHERN REGIONAL RESEARCH LABORATORY

NEW ORLEANS, LOUISIANA

JANUARY 5-6, 1956

FOREWORD

This report is a summary of the information presented at the meeting of the Tung Industry Informal Research Committee held at the Southern Regional Research Laboratory, New Orleans, Louisiana, January 5-6, 1956.

The statements contained in this report of the meeting are those of the speakers and do not necessarily indicate or reflect the views and beliefs of the U. S. D. A.

C O N T E N T S

Summary Report of the Meeting of the Tung Industry
Informal Research Committee
January 5, 1956, at the Southern Regional Research
Laboratory of the Southern Utilization Research Branch,
Agricultural Research Service
United States Department of Agriculture
New Orleans, Louisiana

Five members of the Tung Industry Informal Research Committee, Messr. Lamont Rowlands and Louis Chenel, representing the American Tung Growers Council of America, Messrs. Marshall Ballard, Jr., and R. R. Becke, representing the American Tung Oil Association, and Dr. R. T. Goodwin, representing the National Tung Oil Marketing Cooperative, met at the Southern Regional Research Laboratory, New Orleans, Louisiana, on January 5, 1956, with Drs. C. H. Fisher, G. E. Goheen, A. M. Altschul, L. A. Goldblatt, W. G. Bickford, R. S. McKinney, E. F. Pollard and R. W. Planck; Messrs. E. A. Gastrock, F. G. Dollear, R. L. Holmes, E. T. Rayner; and Mrs. Joan Hoffman of the Southern Utilization Research Branch; and with Mr. Lucien L. Hopper, Jr., Fellow of the National Tung Oil Marketing Cooperative, Inc., Messrs. Jack Greenfield and John McE. Sanderson, National Tung Oil Marketing Cooperative, Inc. Whippany, New Jersey, Dr. Robert Gilman Nelb, Manager, Vibrin Development, Naugatuck Chemical Division, United States Rubber Company, Naugatuck, Connecticut, Dr. W. Lewis Nobles, Professor of Pharmacy, University of Mississippi, Oxford, Mississippi, Mr. George Shannon, Associate Editor, Tung World, Dr. George F. Potter, Horticultural Crops Research Branch, U.S. Department of Agriculture, and Dr. C. A. Murray, Crosby Forest Products Co., Picayune, Miss., to hear reports by members of the Southern Utilization Research Branch, by Messrs. Hopper, Greenfield, and Sanderson of the National Tung Oil Marketing Cooperative, and by Dr. Nelb of the United States Rubber Company on the tung oil research program and to objectively discuss this program. Mr. Julian Saphier, representing the National Tung Oil Marketing Cooperative, Inc., was not present on January 5th due to poor plane connections from New York, but arrived on January 6, 1956 for discussions of most effective cooperation with Southern Utilization Research Branch.

Dr. C. H. Fisher, Chief, Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture, opened the meeting by welcoming those present and stated that it was his conviction that the tung industry is effectively furthering its progress by becoming an active research minded group. Dr. R. T. Goodwin, Chairman of the Tung Industry Informal Research Committee, requested Dr. A. M. Altschul to present the program, and Dr. R. S. McKinney to act as Secretary for the Committee. Dr. Altschul stated that this meeting had three purposes, namely, to review the tung research work, to review the needs of the tung industry, and to assist these needs of industry by providing essential technical information to technical workers in

industry to effectively further the progress of the tung industry. He divided the program into five phases, namely, (1) the chemistry of tung oil; (2) new chemicals from tung oil and tung oil derivatives; (3) polyester resins containing tung oil; (4) new formulations containing tung oil; and (5) the isolation and concentration of the heat stable toxic material in tung meal. A tour of the Laboratory to see this work comprised a part of the presentation program. Dr. Altschul pointed out that a coordinated research program on tung is developing in the industry whereby various groups are benefiting from the mutual exchange of information, thereby speeding the tung program. He stated that as present research forces are spread quite thin, it appears that in certain areas adding another man may quadruple the output. Mr. W. H. Lutz, Vice President and Technical Director of Pratt and Lambert, Inc., a large consumer of tung oil, has stated that they are interested in the chemistry of alpha and beta tung oil, in uses for tung fatty acids and tung derivatives, and in the uses of tung oil as a resin modifier to increase flexibility.

Dr. L. A. Goldblatt summarized the chemical research work carried out on tung oil in the Oil Chemistry Unit along two different lines, involving the chemical modification of tung oil to produce chemical derivatives and the use of tung oil in the production of resinous compounds to extend its utilization. The chemical modification of tung oil, as carried out by Dr. Bickford and Mrs. Hoffmann, included the reactions of tung oil, tung fatty acids, and tung esters in the Diels-Alder reaction with maleic anhydride, propiolactone, acrylonitrile, and similar compounds. Sixteen such compounds have been prepared and are being tested as plasticizers and are being screened for biological activity through the Chemical and Biological Center. Some of these derivatives seem to be satisfactory plasticizers for polyvinyl chloride. The acrylonitrile addition product with tung oil should be relatively economical to produce and is fairly good as a plasticizer. The acrylonitrile adduct of butyl eleostearate is one of the more efficient plasticizers, being distinctly more efficient than dioctyl phthalate, the plasticizer commonly used now, and its other properties are fairly good. Along with the preparation of various Diels-Alder adducts, Dr. Bickford has been carrying out a study of the relative rates of reaction of alpha- and beta-eleostearic acid with these compounds, known as "dienophiles" because they react with eleostearic acid known as a "diene" compound. It was found that in the Diels-Alder reaction, the beta acid always reacts more rapidly than does the alpha acid, but the rate in each case depends on the dienophile. For example, maleic anhydride reacts with the beta acid three times as fast as does the alpha acid, whole chloromaleic anhydride reacts with the beta acid five times as fast as does the alpha acid. Maleic anhydride, on the other hand, reacts about twice as fast as does chloromaleic anhydride. This type of information will be useful to users of tung oil, such as varnish makers and resin manufacturers, who are interested in the rate of reaction of tung oil. These rate of reaction studies

also gives an opportunity to study the affect of a cis or a trans double bond alongside of the pair of trans double bonds in tung oil on the reactivity of the trans-trans diene system; and in addition, by varying the dienophiles, using substituents having positive and negative characteristics, it may be possible to determine whether the rates of reactions depend solely on electronic effects, or whether there is also a spatial effect due to differences in size of the various substituents.

The chemical modification of tung oil also includes the work that Dr. McKinney has been doing on the preparation of monoglycerides from tung oil or eleostearic acid. The practical idea behind this work is the possibility of preparing a fugitive emulsifier, that is a material which is an emulsifier at first and not an emulsifier later on. Such an emulsifier would be very useful. For example, when spraying an emulsion of an insecticide on plants, the insecticide should be well mixed with the water, but should not readily wash off the plants due to rain. It appears that the textile industry has many uses for a fugitive emulsifier of the right kind. One approach was to make crude mixtures of monoglycerides of tung oil using tung oil, while another more basic one is to prepare the pure compound glyceryl monoeleostearate and study its physical and chemical properties. It was found that the usual procedures for preparing monoglycerides by heating tung oil with glycerine and 0.1% sodium hydroxide for three hours at 200° C. yielded 42 percent monoglycerides, but destroyed about half of the eleostearic acid in the crude monoglycerides. Tung oil monoglycerides containing about 25 percent of monoglycerides have been prepared without significant destruction of the eleostearic acids in the monoglycerides were prepared by heating anhydrous tung oil and glycerol for two hours at 60° C., using 1.0 percent sodium methoxide as catalyst. A product containing about 75 percent monoglycerides of tung oil has been prepared by using sodium methoxide as catalyst and pyridine as solvent. The analysis of the products for monoglyceride content proved quite difficult, as the usual methods for determining monoglycerides gave erratic and frequently erroneous results. However, a reasonably satisfactory method for the determination of glycerol monoeleostearate has been devised. Tung oil monoglycerides have been fractionated using various solvents, but this method has proved unsatisfactory for obtaining pure glycerol monoeleostearate. The addition of tung oil monoglycerides to oils like cottonseed oil lowered their interfacial tension to water very substantially. The addition of 2% of tung oil monoglycerides to cottonseed oil lowered its interfacial tension against water by 90%, making it much easier to emulsify with water.

Work is being carried out by Mr. Lucien Hopper, Jr., Fellow of the National Tung Oil Marketing Cooperative, Inc., on surface coatings. Mr. Hopper has shown that a resinous ingredient such as zinc resinate can be used to control polymerization and avoid the gelation of tung oil. This work forms the basis of a patent application which has been

filed in the Patent Office. He has carried out pioneering work on the use of epoxy resins using tung and tall oil fatty acids in varying proportions. This pioneering work of Mr. Hopper has interested officials of the Shell Chemical Company in the use of tung oil fatty acids with their "Epon" resins and has influenced them to alter their recommendations with respect to the use of these resins, especially in conjunction with tung oil. Mr. Hopper has also demonstrated the feasibility of using a safflower-tung oil vehicle as a non-resinous house paint, obtaining a more flexible, durable paint vehicle than is obtained with one containing resin. He found that tung oil containing vehicles prepared using tripropionin had fungicidal properties, as Miss Ruth Mayne of the Southern Utilization Research Branch has found by laboratory microbiological tests.

Mr. John McE. Sanderson next spoke on the promotional efforts of the National Tung Oil Marketing Cooperative, Inc. He referred to the report of the Battelle Memorial Institute showing that before and after World War II about 100 million pounds of tung oil was used annually in the United States, but in recent years only about 50 million pounds was used. During the period of scarcity and high price of tung oil, substitutes have been found, and its use reduced to the irreducible minimum. Consumers report that even this "irreducible minimum" will be further reduced if they cannot secure adequate supplies of tung oil at a price which will permit tung oil to compete in use with other materials. It is still used to meet Government and industrial specification, in spar and floor varnishes and in miscellaneous items, but where previously 70 percent tung oil was used, about half that amount is now used. It appears that even if the supplies of tung oil are ample and the price is lower, only about 60 million pounds would go into present uses. Alkyds using soybean oil have been used to replace tung oil in four hour enamels. Tung oil together with tall oil can be used in alkyds, but the paint and varnish industry, with few research laboratories, need help in using such new materials. Tung oil modified phenolic resins are being used for impregnation of laminates for punch stock, expecially as backing for printed electrical circuits for radios and other electronic equipment to obtain toughness. It appears, however, that the industry needs new uses for tung oil, such as its use in polyester resins which the U. S. Rubber Company is now investigating, which will help the situation, not so much this year, but in the following year and in the years that follow. Experiments have been started wherein tung oil has been subjected to several types of irradiation in the development of a long range future for tung oil. Mr. Jack Greenfield will give some details of these irradiation tests and of the work he has been doing in the laboratory to help consumers utilize tung oil to the best advantage and to develop new tung oil products.

Mr. Jack Greenfield stated that their Tung Topics aims to accomplish a three fold purpose, namely, to review old methods of using tung oil for newer workers in the field, to expand the use of tung oil in modern

formulae, and to publicize new research and developments on tung oil. He stated that although soybean oil is largely used in alkyd resins, tall oil is being used more frequently as the fatty acid ingredient and, when used with tung oil, does not suffer from "after tack" which occurs if only refined tall oil is used. They have also been working on "epon"-tung oil vehicles and have found that the addition of para tertiary butyl benzoic acid to the vehicles imparted a greater hardness to the films. They have prepared and used the methyl ester of tung oil in protective coating films. The methyl ester is a liquid and therefore easier to handle than the solid tung oil fatty acids. They can be used instead of the acids for esterification and have some value as a plasticizer. For example, tung oil and its methyl ester reacted with poly-butadiene can be baked for 15 minutes at 300° F. to a flexible, highly chemical resistant film suitable for can linings. Tung oil methyl ester reacted with pentaerythritol to form a medium length alkyd which cures at 300° F. in 15 minutes to a very hard baked surface, similar in hardness to that obtained with the melamine resins. Hydroxylated tung oil reacted with isocyanates yielded excellent films and foams. Tung oil was bombarded with gamma rays equivalent to 763,000 Roentgens per hour for 24 hours, with no massive formation of beta oil and no notable change in refractive index, iodine numbers, or viscosity. When bombarded with high energy electrons, using doses as high as 40 million Roentgens, the refractive index was lowered, the viscosity raised, beta formation and gellation occurred as the dosage was increased.

On the tour of the Laboratory, Messrs. Holmes and Rayner demonstrated and illustrated the methods used to separate and concentrate the heat-stable ether-soluble toxic ingredient of tung meal, in order to determine its composition, to develop a practical method for detoxifying tung meal, and to devise a method for analyzing tung meals for toxins. Mr. Hopper showed the results of his formulation work to prevent the gelation of tung oil, and in the use of tung oil in epon resins, in mildew resistant vehicles, in a "non-resin" tung oil paint and answered questions in regard to this work.

Dr. Bickford and Mrs. Hoffman described their work in preparing tung oil derivatives with dienophiles, and on the use of the acrylonitrile adduct of butyl eleostearate as a plasticizer for polyvinyl chloride. They also presented information obtained regarding the fundamental nature of alpha and beta eleostearic acid and the rates of their reactions with various reagents. Dr. McKinney then described the preparation of tung oil mono-glycerides by three procedures, the methods used to separate the pure mono-glycerides from the crude products, and the effect of tung oil mono-glycerides on the surface tensions and interfacial tension of oils and water.

Continuing the meeting, Dr. R. G. Nelb described the work which the U.S. Rubber Company is doing for the Southern Utilization Research Branch under contract on the use of tung products in polyester resins. Tung oil is not compatible with polyesters such as polypropylene glycol-maleate-phthalate, causing turbidity, accelerating gelation and decreasing exothermic heat. Tung fatty acids are compatible but retard gelation. A polyester containing combined tung oil shows increased viscosity, permitting more styrene to be used, but above 15 percent tung oil there is a great tendency toward gelation. The presence of any unreacted eleostearic groups accelerates gelation and reduces the exotherm, like tung oil itself. For example, a resin containing 5 percent tung oil gelled in 15 minutes and the temperature rose to 138° C. in 11 minutes. The same resin reacted with 25 percent tung oil (only partial combination) gelled in 11 minutes and the temperature rose to 37° C. in 35 minutes. Hardening was slow but progressive. It was found that the maleic group when present as maleic anhydride, reacts very readily with tung oil, while the fumaric group, as acid or ester, reacts slowly. However, at 200° C., diethyl maleate showed practically no reaction, while diethyl fumarate reacted at about the same rate as fumaric acid, indicating that when tung oil is reacted with an already formed alkyd, the reaction will consume the fumaric unsaturation in preference to the maleic unsaturation. This would produce a resin which would co-polymerize slowly, since fumaric unsaturation co-polymerizes much more readily than maleic unsaturation. Resins have been prepared using up to 10 percent tung oil in the alkyds. The alkyds used have been prepared using ethylene glycol or propylene glycol with phthalic anhydride and maleic anhydride and phthalic anhydride and fumaric anhydride. Clear castings of these resins have been tested for tensile elongation, hardness, water absorption, and falling ball impact. The results indicated little change in physical properties with increase in tung oil, except perhaps embrittlement with increase in tung oil, but these results must be checked.

Mr. Marshall Ballard, Jr., President of the American Tung Oil Association and a member of the Oilseed and Peanut Advisory Committee of the U. S. Department of Agriculture, spoke on the problems and needs of the tung industry. As stated in a recent letter to Mr. J. D. Lawrence, President of the Bank for Cooperatives in the Southeastern United States, Mr. Ballard said that it was his opinion that, in spite of the crop failures in the last two years, the future of the tung crop looks good. It is the best cash crop in most sections where it is grown, but profits will depend upon the yield of oil per acre and the efficiency of the orchard operation. However, it appears that the ultimate success of tung operations will also depend upon the research efforts being made by the tung industry, the National Tung Oil Marketing Cooperative, the American Tung Oil Association, and also the Southern Utilization Research Branch of the U. S. Department of Agriculture aimed at developing new and more profitable uses for tung oil and its by-products, thereby expanding their markets. With about 9 to 10 million pounds of tung oil in consumer's hands, 15 to 16 million pounds in CCC stocks, about 2 million pounds of

oil produced from the 1955 domestic crop, and about 25 million pounds of tung oil imported from South America, there will be about 52 to 53 million pounds of oil available for the current marketing year. With an annual consumption of about 50 million pounds of tung oil, it is apparent the supply situation for tung oil for this year will be extremely tight.

Dr. L. A. Goldblatt gave a report in regard to the Federal and A.S.T.M. Specifications for tung oil. After considerable discussion, it was agreed that the Federal Specifications for tung oil should be made to agree with the A.S.T.M. Specifications for this commodity. A motion picture, entitled "The Story of Tung" furnished through the courtesy of the Crosby Forest Products Company, Picayune, Mississippi, was then shown. The meeting was then adjourned.

RESEARCH ON TUNG OIL IN THE OIL CHEMISTRY UNIT

L. A. Goldblatt

In the Oil Chemistry Unit we have been carrying on work along two essentially different lines. These are (1) the chemical modification of tung oil or tung oil acids to produce chemical derivatives and (2) the production of various resinous compositions. The work on chemical modification in turn has followed two lines -- one carried out by Dr. Bickford and Mrs. Hoffmann involves the chemical modification of the double bonds of the eleostearic acid which is the chief component of tung oil, and the other carried out by Dr. McKinney at Bogalusa on modifying the carboxyl end of eleostearic acid. That is the other important functional group in tung oil.

Dr. Bickford's work has involved particularly the addition of whole molecules of other compounds to tung oil by what is known as the Diels-Alder reaction. Eleostearic acid is what is known technically as a diene and compounds known as dienophiles, literally diene lovers, react with dienes by the Diels-Alder reaction. There are many dienophiles, and Dr. Bickford and Mrs. Hoffmann have carried out reactions with such dienophiles as maleic anhydride, chloromaleic anhydride, propiolactone, acrylonitrile, fumaronitrile, benzoquinone, and others using tung oil or various esters of eleostearic acid and have screened the products particularly for suitability as plasticizers for polyvinyl chloride. About 16 different derivatives were screened. I won't give you all the data - most of it is quite technical and has either been published or is going to be published. It is sufficient to say that some of them seem to be satisfactory plasticizers for polyvinyl chloride. One I might mention particularly is the acrylonitrile addition product with tung oil. That ought to be relatively economical to produce, and is fairly good as a plasticizer. The acrylonitrile adduct of butyl eleostearate is one of the more efficient plasticizers. It is distinctly more efficient than dioctyl phthalate which is the plasticizer that is commonly used now and the other properties seem fairly good. All of the Diels-Alder products were submitted to the Chemical and Biological Coordination Center for screening for biochemical activity but there is nothing particularly significant to report on their results as of now.

Along with the preparation of various Diels-Alder adducts, Dr. Bickford has been carrying out a study of the relative rates of reaction of alpha- and beta-eleostearic acid with various dienophiles. The results are very interesting although perhaps a little technical. He found, for example, that in the Diels-Alder reaction the beta acid always reacts more rapidly than does the alpha acid but how much more rapidly depends on the dienophile. It isn't always the same. For example, with maleic anhydride the beta acid reacts about three times as fast as does the alpha acid, at the same temperature. But with chloromaleic

anhydride the beta acid reacts about five times as fast as does the alpha acid. In turn, maleic anhydride reacts about twice as fast as does chloromaleic anhydride. This kind of information ought to be useful to people that are interested in the rate of reaction of tung oil and that means varnish makers, resin manufacturers, and in general anybody that reacts tung oil. That is one reason Dr. Bickford is doing this rate work. Another reason is that in the two eleostearic acids we have an unusual opportunity for studying a particular kind of chemical configuration. Each of the acids has a pair of trans double bonds, which makes them dienes, but one has alongside a cis double bond and the other has alongside a trans double bond. This presents a unique opportunity to come to some understanding of how a cis bond affects the reactivity of the trans-trans diene system. Another reason for studying the rates is that by varying the dienophiles he might be able to relate the influence of various substituents having positive or negative characteristics on the rate of reaction and see if the differences in rates can be accounted for solely on the basis of electronic effects -- that is, the electrical nature, or whether there is also a spatial factor due to the difference in size of the various substituents.

Dr. Bickford will tell you more about his work when you get downstairs in the tour of the Laboratory.

Dr. McKinney has been working on the preparation of monoglycerides from tung oil or eleostearic acid. The practical idea behind this work is the possibility of having a fugitive emulsifier, that is a material which is an emulsifier at one stage of the game and not an emulsifier at a later stage. Such a thing would be very useful, for example, when spraying an emulsion of insecticide on plants. You want the insecticide to be well mixed with the water but you don't want it to wash off the plants right away. The textile industry has a great many places where they could use fugitive emulsifiers of the right kind. So one approach was to try to make crude mixtures of monoglycerides of tung oil using tung oil itself and another more basic one is to prepare the pure compound glyceryl monoeleostearate and study its physical and chemical properties. Unfortunately, the usual ways for making monoglycerides will not work with tung oil, and the usual methods of analysis will not work because of the peculiar unsaturation in tung oil. For example, the standard way of making a monoglyceride is to cook the oil with glycerine and 1% NaOH for a couple of hours at 200° C. You cannot do that with tung oil because although to be sure you get a monoglyceride it is not the monoglyceride you want because in the process of cooking for a couple of hours at 200° C. you destroy the eleostearic acid. Again Dr. McKinney will tell you the details but I will say now that progress has been made in getting increased concentration of monoglycerides relatively rich in eleostearic acid and in making pure glyceryl monoeleostearate. Also, that tung oil monoglycerides lower the interfacial tension of oils like cottonseed oil against water very substantially. The addition of 2% of

tung oil monoglyceride to cottonseed oil lowers the interfacial tension against water by 90%. That means that the cottonseed oil would be much easier to emulsify with water. Another very interesting thing brought out is that the interfacial tension of tung oil against water seems to be extremely high. Dr. McKinney got a value of about 60 dynes at 25° C. For cottonseed oil it is about 15 dynes. That result needs checking but if it is correct, it is extremely interesting and is certainly something that none of us expected.

The resin work, too, is divided into two parts. One is being carried out by Mr. Lucien L. Hopper who is the Fellow of the National Tung Oil Marketing Cooperative, Inc., on surface coatings stationed at SURB and the other is being carried out under contract with the U. S. Rubber Co. under the supervision of Dr. Nelb.

Mr. Hopper has made a great deal of progress in a very short time and I will refer very briefly to just four items.

First. He showed how a resinous ingredient such as zinc resinate can be used to control polymerization and avoid gelation. That forms the basis of a patent application which has been filed in the patent office.

Second. He has carried out pioneering work on the use of epoxy resins such as the Shell's Epons or Dow's Resin 622 with varying proportions of tung oil fatty acids diluted with fatty acids such as tall oil fatty acids all the way from 50-50 to about 98% - 2%. The Shell people are very much aware of the pioneering work that Mr. Hopper is doing here and are greatly interested in it.

Third. Mr. Hopper has demonstrated the feasibility of using a safflower-tung oil vehicle as an all oil (no resin) vehicle for exterior house paints. I do not know anything about paints but Mr. Hopper tells me that if you put an ordinary resin in a house paint vehicle, it becomes too brittle for good durability so that an all oil (no resin) house paint vehicle is very desirable.

Fourth. He has made real progress in taking advantage of the almost excessive reactivity of tung oil to introduce other specific desirable properties. Specifically, by using propionic acid to replace some of the tung oil acids he has a built-in fungicide that seems to be very effective in preventing mildew. Miss Ruth Mayne of this Laboratory has carried out the mildew resistance tests and the products resist mildew quite well. You will see some of the results of these tests in Mr. Hopper's laboratory downstairs.

Finally, just a word in connection with tung oil in polyester resins. After a great many vicissitudes that contract was finally awarded to the U. S. Rubber Company in October. Also after a good many vicissitudes Dr. Nelb managed to get a plane to New Orleans to tell us about it. I shall leave that all to him except to say that in a letter to me some time ago he wrote that "the progress of the research contract work seems promising".

RESEARCH ON TUNG MEAL

R. W. Planck[1/]

One phase of our tung research has the goal of increasing the usefulness and value of the meal. Tung meal, as now produced, contains two types of toxic substances, each of which is capable of making the meal too toxic for use in animal feeds. Consequently the meal is sold at very low prices for use as fertilizer and does not contribute much to the value of the tung crop.

Our tung meal investigations at the U. S. Tung Oil Laboratory in Bogalusa, Louisiana, are directed toward learning the chemical properties, the chemical reactions and the composition of the one of those toxic fractions which is soluble in alcohol, ether and other organic solvents. Fresh tung meals are freed from oil and extracted with ether or acetone to give crude solutions of the toxin. These crude extracts have been concentrated further by taking up the solids successively in petroleum ether and then in acetone. Further concentration was accomplished in a Craig counter-current liquid-liquid extractor in which it was found that the toxic materials remained in the alcohol (80%) layer while impurities were removed in petroleum ether. As little as 10 milligrams of a fraction prepared in this way is capable of killing one week-old chicks.

A multitude of chemical tests have been carried out on the toxic fractions with the aim of learning the composition and the reactive groups in the toxic molecules. These tests have established that the material is a solid composed of carbon, oxygen and hydrogen. It gives positive tests for the presence of ester linkages, double bonds, and carbonyl groups. In many ways its reactions suggest a structure of, or similar to, an unsaturated lactone.

Crude extracts of this toxic material appear to be fairly stable to air, heating, and contact with acids. Their toxicity to chicks is reduced slowly on standing at room temperature or quite rapidly whenever the extracts are heated with alkalis such as ammonia or sodium hydroxide. This clue to an effective method of detoxification will be followed up in future work.

Efforts to obtain really pure compounds (toxins) have not been completely successful yet. There are indications that the nearly pure fractions undergo chemical degradation while under test. Use of the new methods of paper chromatography using glass paper impregnated with silicic acid has indicated that the concentrated toxins are either mixtures or that they are decomposing as they move up the paper. Efforts to further purify the Toxins are yielding preparations that, according to chick feeding tests, are more toxic than those previously prepared.

1/ This was presented as part of general discussion by A. M. Altschul but is put here in greater detail for convenience of committee.

Progress in the testing of these tung extracts has been made by Dr. A. B. Watts and his group in the Department of Poultry Industry at Louisiana State University, Baton Rouge, La. They have found that sub-lethal dosages of these extracts cause week-old chicks to stop eating and lose weight. The extent of the weight loss and the length of time before the chick starts to gain again are measures of the toxicity of the sample.

Plans are underway for the use of these facts in the investigation of methods for the complete detoxification of tung meal into a product that will be safe for use in animal feeds and that will bring a larger monetary return to the tung industry.

PROMOTIONAL EFFORTS OF THE NATIONAL TUNG OIL MARKETING COOPERATIVE, INC.

J. McE. Sanderson

Since March 1st I have been around most of the east and north contacting the technical men in the paint industry, together with other actual or potential consumers of tung oil, to see what can be done to retain and extend its older uses, and trying to stimulate development work on its application in new fields. The situation we are up against can be summarized about as follows:

Prior to, and immediately following, World War II this country used an average of a little over 100,000,000 lbs of tung oil per annum most of which came from China. In the past five years this has gone down to half of that in spite of the growth since the war of the paint and other consuming industries. This big drop in usage has been due to a combination of commercial and technical factors, both of which must be considered in our efforts toward future expansion.

Because, in the past 15 years, supplies of tung oil have at times been limited and price appreciably higher than other drying oils, consumers have scrutinized their formulas and tried wherever feasible to replace tung oil with other materials. Unfortunately for its producers, tung oil has been found by many consumers to be not as essential for some of their products as they formerly thought. Furthermore, they tell me that the "irreducible minimum" they have now attained will be still further reduced if they again cannot secure adequate supplies at a cost which permits tung oil to compete in use with other materials.

Coatings in which tung oil continues to be used may be roughly grouped as follows:

(1) Formulas set up to meet definite specifications, on composition or on performance characteristics, which can only be attained with tung oil. These include such things as military coatings, can liners, etc.

(2) Spar, floor, and other varnishes where most manufacturers are now using much lower proportions of tung oil than formerly --- they know that quality has suffered but they are"getting by"with their customers.

(3) Miscellaneous items made in volume too small to justify the time and expense of formula revision.

I have listened to a wide variety of opinions regarding the possible effect of future availability in ample quantities at a relatively low price. One paint maker told me recently he would use five times as much

as his current consumption, others say it would have no effect. After listening to them all I would estimate that under such conditions we might see a 20-25% increase in these old uses. This would mean jumping from 50 to 60 million pounds, an increase not to be sneezed at but still far below the old 100 million --- so price and availability alone are not the answers to our problem.

The big change has of course been technical, not replacement of tung oil with cheaper oils (though some of this has happened), but the use of new things instead of tung oil varnishes. We used to think it essential to use tung oil to make quick drying durable finishes but a wide variety of other products are now available for that purpose. Most "4 hour" enamels are now made with alkyds, flat wall paint vehicles containing tung oil have been replaced by alkyds or latices, trim and deck paints are now reinforced with alkyds rather than tung oil varnishes. Low price won't reverse this trend, so (if you can't lick 'em, join 'em) we're promoting the incorporation of tung oil in both alkyds and co-polymers. In the former we have made some small but definite progress, especially with combinations of tung oil with tall oil or tall oil fatty acids, although here we are limited by the relatively poor color retention of tung compared to soya oil. Several labs say they are investigating use of tung oil or tung acids in copolymer latices, but nothing seems to have resulted to date and specific help from the Southern Regional Research Laboratory, would be welcomed. Even a small percentage of tung oil in latex paints could mean large volume.

At least one application outside the paint field seems to be growing, namely tung oil modified phenolic resins for the impregnation of laminates for punch stock, especially as backing for printed electrical circuits for radios and other electronic equipment. It is still uncertain how far tung oil will compete with dibutyl phthalate and other plasticizers, but it looks as though this field might utilize 1-2 million additional pounds of tung oil per year.

Our big need appears to be for some completely new applications such as the polyester resins which U. S. Rubber Co. is now exploring --- 5% tung oil in the current total would mean another 3,000,000 lbs per year of tung oil. It could even be several times that amount as the reinforced plastics industry grows, or as tung oil might solve current problems in the use of polyester resins to make pipe or surface coatings.

Among our efforts to stimulate consumers to look beyond their immediate problems and include tung oil in their developments for the long range future, we are trying to get them to think of the application of nuclear energy. This may look like blue sky at the moment, but it is something which I am sure neither we nor the paint industry can afford to neglect in view of work underway in this field by practically every important firm in the plastics, rubber, petroleum, and chemical industries. So, we have already started some experiments on subjecting tung oil to several types of irradiation and feel that publication of our results will serve to induce some of our tung oil consumers to carry the ball further.

I will leave it to Jack Greenfield to give you some details of our irradiation tests and of what he is doing in our laboratory to help consumers utilize tung oil to best advantage and to develop new tung oil products for them. We hope to expand this work and will continue to keep the trade advised on our efforts thru "Tung Oil Topics" with which you are all familiar.

In these brief comments I have tried to present a realistic picture which will point up the seriousness of the problems with which we are faced. The consuming trades are hungry for suggestions on how they can utilize tung oil in products which they can sell at a profit. The National Tung Oil Marketing Cooperative is very appreciative of the efforts which this group is making in that direction.

THE WORK OF THE RESEARCH LABORATORY OF THE NATIONAL TUNG OIL MARKETING COOPERATIVE, INC.

Jack Greenfield

Tung Topics is published to accomplish a 3 fold purpose:

1. Review old methods of using tung oil for the newer workers in the field.

2. Expand the use of Tung oil in modern formulae.

3. Publicize new research and developments on Tung oil.

Some of our recent work covering parts (1) and (2) above are the preparation of:

A. Tung - Tall oil alkyds. Tall oil is being used more frequently as the fatty acid ingredient in alkyd resins because of its low cost. However, its one bad disadvantage is the after tack it imparts to a dried film. We have successfully demonstrated that Tung oil will overcome this tack.

B. Epon - Tung acid vehicles. Our work differed slightly from Mr. Hopper's in that we used a substantial portion of para tertiary butyl benzoic acid in our vehicles to impart a greater hardness to the films.

Some of the newer work coming under the heading of (3) above is:

A. Utilization of the Methyl esters of Tung oil. We have been working with these esters for several months now from the standpoints of studying better methods of preparation and of using the ester in protective coating vehicles. Our interest in the methyl ester stems from the facts that (1) it is a limpid liquid and therefore easier to handle than fatty acid which is solid at room temperature; and (2) it is more stable than the fatty acid. The methyl ester can be used wherever the acids are required for esterification and in addition the esters are of some value as a plasticizer. For example, polybutadiene can be plasticized with the methyl ester in the ratio of 75% polybutadiene and 25% methyl ester. A vehicle of somewhat lower cost can be made from 50% polybutadiene, 45% Tung oil, and 5% methyl ester. These mixtures can be baked for 15 minutes at 300° F. to a flexible, highly chemical resistant films suitable for can liners.

The methyl ester can be also used in the making of alkyd resins, because the gelling tendency that is characteristic of the oil at high temperatures is reduced. This is illustrated by the experiment where we prepared

an all tung alkyd using pentaerythritol in a medium oil length resin. An alkyd is impossible to prepare with the oil. The alkyd cures at 300 ° F in 15 minutes to a hardness similar to that obtained from melamine; but it does not air dry too well since some methyl ester remains unalcoholyzed in the film and acts as a very slow drying plasticizer.

B. Hydoxylation of Tung oil. Of the approximately 2.5 double bonds per Tung acid molecule, we believe that we have hydroxylated 0.8 double bonds. If the hydroxylation is carried higher, then the product is insoluble in all solvents and water. We are investigating further the excellent films and foams obtained by reacting the hydroxylated materials with diisocyanates. We expect to examine the physical properties of epoxidized Tung oil for some possible commercial use.

C. Several attempts were made to prepare vinyl acetate emulsion copolymers with a bodied Tung oil. Excellent adhering and water resistant films were obtained but more work will be required to raise yields.

D. Atomic Radiation Experiments. We are making several series of experiments. It is our intention to expose the bulk oil to gamma, high energy electron, and neutron radiation. The gamma rays are obtained from Cobalt 60. The high energy electrons are obtained from the General Electric resonance transformer, and the neutrons are obtained from the neutron flux in the center of the Uranium pile located at Brookhaven National Laboratories. The oil is to be analyzed before and after the radiation experiments. Thus far we have subjected the oil to the gamma rays and to the high velocity electrons.

The oil was subjected to a dosage of gamma rays equivalent to 763,000 roentgens per hour for 24 hours. Thus far we have detected no change in iodine number, refractive index, and viscosity. Moreover, we have detected no massive beta formation in the oil. The electron beam however, raised the viscosity, lowered the refractive index, caused beta formation, caused gellation, as the dosages were increased. The specimens with increased viscosity dried rapidly but with a frosty film. Our experiments have not progressed far enough to make any predictions.

TUNG OIL AND TUNG OIL DERIVATIVES WITH POLYESTERS

R. G. Nelb

The initial work on the use of tung oil and tung oil derivatives with polyesters has constituted an examination of the following subjects:

A. Miscibility of tung oil with polyesters. Tung oil is not compatible with polyesters such as polypropylene glycol-maleate-phthalate. The addition of as little as 1% gives turbidity. Tung oil mixed with a polyester accelerates gelation and decreases exothermic heat.

Tung oil acids are compatible but in contrast to the oil, the acids retard gelation. An alkyl eleostearate such as methyl eleostearate would be expected to be miscible and show the same effects as a glyceride.

B. Effect of combined tung oil. The polyester containing combined tung oil shows an increased viscosity permitting more styrene to be used. Above 15% tung oil, there is a great tendency towards gelation. If there are any unreacted eleostearic groups, the effect of gelation is similar to that of tung oil itself (gelation accelerated and exotherm reduced). For example, a resin containing 5% tung oil gelled in 15 minutes and the temperature rose from room temperature to 138° C. in 11 minutes. The same resin reacted with 25% tung oil (only partial combination) gelled in 11 minutes and the temperature rose to 37° C. in 35 minutes. Hardening was slow but progressive.

C. Comparison of reactivity of maleic and fumaric groups with tung oil. Maleic and fumaric groups have different reactivities with tung oil, maleic reacting very readily while fumaric is relatively slow. At 200° C. diethyl maleate showed practically no reaction while diethyl fumarate reacted at about the same rate as fumaric acid itself. This preliminary work might indicate that when tung oil is reacted with an already formed alkyd, the reaction will consume the fumaric unsaturation in preference to the maleic unsaturation. This would tend to produce a resin which would copolymerize with styrene slowly, since fumaric unsaturation copolymerizes much more readily than its maleate unsaturation.

D. Resin preparations. To date resins have been prepared using up to 10% of tung oil in the alkyds. The alkyds used have been prepared using ethylene glycol or propylene glycol with phthalic anhydride and maleic anhydride and phthalic anhydride and fumaric acid.

Clear castings of these resins have been measured for tensile elongation, hardness, water absorption, and falling ball impact. The results indicate little change in physical properties with increase in tung oil. The falling ball impact test does indicate possible embrittlement with increase in tung oil, but these results must be rechecked.

TUNG OIL SPECIFICATIONS

L. A. Goldblatt

Federal specifications for tung oil are being reviewed and we have been asked to assist in reviewing the specifications for amendment or revision.

There is considerable confusion between a specification set up primarily to meet the service requirements of a consumer and a standard of identity set up primarily to ensure absence of adulteration. This is especially the case for Federal specifications where the layman might well consider that a Federal specification for a commodity like tung oil to satisfy should be such that any authentic, unadulterated tung oil should meet the specifications - even though they might not meet service requirements.

Federally purchased tung oil is used almost invariably to produce derived products such as vehicles or resins, and we do not know what the minimum service requirements are for the tung oil used in these products. The American Society for Testing Materials has recently revised its specifications for tung oil. All segments of industry, producers as well as consumers, are represented on ASTM Committees which set up specifications for tung oil. The Federal Government generally uses tung oil for the same general purposes that industry does. It would be desirable to have a single set of specifications for tung oil, rather than a dual set - one for private industry and a different one for government.

A great deal of data was obtained on the properties of 22 American tung oils produced in 1950-51 and 28 oils produced in 1951-1952. All 22 of the oils produced in the 1950-51 season would have met Federal specifications. However of the 28 oils of the 1951-1952 season, all apparently authentic tung oils, 10 would have failed to meet ASTM specifications in at least one respect. Another property being scrutinized is the concentration of beta oil. The amount of solid in tung oil is apparently of some concern to some people. Present specifications, both Federal and ASTM, only require that the oil shall be clear and free from sediment and suspended matter at 65° C. An authentic tung oil, even if completly converted to the beta form would be clear at this temperature.

After considerable discussion it was recommended that Federal specifications for tung oil should be made to agree with ASTM specifications for this commodity.

STATUS OF THE TUNG INDUSTRY

Marshall Ballard

I hope all of you appreciate the fact that any approach to the subject of the nature of that which Dr. Altschul has asked me to comment upon today is tenuous at best. In any estimate or appraisal of this kind, there are marginal areas for honest differences of opinion. In preparing this report, however, I am setting forth not only my own honest personal opinions as accurately as I can portray them to you, but also my conclusions drawn as a result of numerous discussions of the subject with many tung producers, large and small, as well as with technical people like Dr. Potter and others in the Agriculture Department, as well as technical people and business men in the consuming industries.

In addition to the backers just referred to, I have also had occasion to discuss the matter with several other leading backers, who have an uncanny knack of probing deeply and getting the basic facts and conditions.

Here are my observations, therefore, for what they may be worth:

I would say quite frankly that the future of the tung industry still looks good. I believe an objective appraisal would reveal that tung is still the best cash crop in most sections of the tung belt where it is grown, in spite of the setbacks it has had lately at the hands of the weather. Of course, most of us in the tung industry today realize the urgent need for greater and more substantial diversification in our tung farming operations than has heretofore been practiced. I am happy to say that many of us are diversifying our operations more than ever before and we feel that this will lend greater stability to the whole industry in the long run.

Tung's future will depend a great deal on the extent to which the industry is able to get production costs down in the face of rising prices on materials which the tung grower needs to produce his crop and falling tung prices, which are declining in line with prices on other competitive oils. The ultimate success of the industry will also depend upon the outcome of the research efforts which are being made, not only by the industry itself, through its National Tung Oil Marketing Cooperative, and the American Tung Oil Association, but also by the U. S. Department of Agriculture thru its Regional Research Laboratory at New Orleans. The research to which I refer is specifically utilization research aimed at developing new and more profitable uses for tung oil and the by-products of tung oil production, in order to expand the markets for tung oil and its by-products.

In view of the fact that the surface has just been scratched on this research front, when coupled with the fact that tung oil is still considered

to be the top vegetable drying oil in existence today, leads many of us to feel that these research efforts offer much promise of ultimate success.

I am sure you are aware of the fact that many developments have been made in vegetable oil technology over the past fifty years. A great deal of information has been gained in the last fifteen or twenty years on how to convert one vegetable oil into another by chemical treatment, due to the fact that most of the available oils known today consist essentially of mixtures of the same fatty acids in varying proportions. For this reason price is largely the determining factor as to which oil a consumer may use as his starting raw material.

The tung industry, aided greatly by the U. S. Department of Agriculture and some of the State Experiment Stations, has made great strides in the last twenty years in the development of new and higher yielding varieties through variety selection. Over this same period it has also developed a much more improved and economical method of cultivation, fertilization, et cetera, all of which have worked in the direction of increasing per-acre yields and lowering unit costs of production.

While continuing to devote its attention to these matters, the industry must now turn to utilization research to meet competition, if it is to hold its present market and develop new markets. So far, the tung crop failures the industry has suffered in recent years have had little effect toward dampening the enthusiasm of growers over the prospect of ultimate success as an industry. Many growers in various parts of the belt have suffered over the last two years. They still seem, however, to be optimistic about the future and to be able to find the necessary financial means to carry on their operations on a basis consistent with the losses they have suffered.

In this connection, I am sure a lot will depend on the outcome of the 1956 crop, relative to whether or not we have another freeze or frost-out of that crop. You understand, of course, that the loss of the 1955 tung crop was due to a most unprecedented freeze occurring on the night of March 27 at temperatures lower than any which has been experienced up to that time in the annals of the U. S. Weather Bureau. The tung crop had already escaped what would normally be considered as a frost-out and the nuts were already on the trees when the freeze of late last March struck and destroyed practically the entire crop, along with practically every other fruit and truck crop in the Southeastern United States that was growing at the time the freeze occurred.

At present prices the amount of net profit that may be expected from growing and processing a tung crop is dependent in part upon the yield of oil per acre that may be expected from a given orchard, and partly upon the farmer and how efficiently he has operated during the year. In connection with the latter factor, some tung farmers have very little after expenses are paid. Others show worthwhile gains.

On the basis of present tung prices (about 23¢ per pound of oil), I would say that a grower would have to make a crop of at least one and one-half to two-tons per acre of tung nuts, averaging 18-1/2% oil content or better to make what may be considered as a reasonable profit.

As stated above, the amount of net profit is dependent in part upon the yield of oil per acre. This yield in turn is dependent upon varieties of trees in the orchards and conditions under which they are grown, such as fertilizer and cultivation practices and the like.

With some of the newer selected varieties of trees and recommended fertilization and cultural practices, and proper milling efficiency, a yield of one and one-half to two-tons of tung nuts per acre may be expected to produce 525 to 700 pounds of oil per acre. Even at the present support price, which incidentally is three to four cents under the current open market, this kind of yield should produce gross per-acre income of $105.00 to $140.00 per acre. At this level of gross income a reasonable profit may be expected, provided the farmer himself managed his operation efficiently.

An analysis would have to be made, therefore, of each orchard to determine its productive capacity from the standpoint of both present and future potentials before a safe and sound evaluation of any given tung orchard and its profit potential might be made.

As the situation, supplywise, now stands, from the standpoint of total available supplies from all sources, both domestic and foreign, exclusive, of course, of Red China against which an embargo by this country now exists, it appears that it is going to be "nip and tuck" to fill the needs of U.S. consumers, based even upon their present level of annual consumption of tung oil.

At this writing an estimated 9 to 10 million pounds of oil is left in private consumer's hands. Approximately another 15 to 16 million pounds remain in CCC stocks, and best estimates indicate that not over 2 million pounds of oil will be produced from the 1955 domestic crop on account of this year's severe freeze-out. It is estimated that not over 25 million pounds will come from foreign sources, principal of which are Argentina and Paraguay, during the coming marketing year, which began November 1 just past. This makes a total available supply for the current marketing year, which has just begun, of approximately 52 to 53 million pounds, as against a current annual consumption of some 50 million pounds.

It may readily be seen, therefore, that the outlook on tung oil, supply-wise, for the next twelve months is extremely tight. In view of the above supply outlook, and barring any future opening of U. S. gates to Chinese oil, it may readily be seen, therefore, that the prospects for selling the 1956 domestic crop, should there be one, should be extremely good.

That, is the picture as I see it today.

Meeting of the
TUNG INDUSTRY INFORMAL RESEARCH COMMITTEE
at the
Southern Regional Research Laboratory
New Orleans, Louisiana

January 5, 1956

ATTENDANCE LIST

Visitors

Ballard, Marshall, Jr., American Tung Oil Association, Lumberton Mississippi
Becke, Roland, American Tung Oil Association, Poplarville, Mississippi
Chenel, Louis, Tung Growers Council of America, Covington, Louisiana
Goodwin, R. T., American Tung Oil Association, Poplarville, Mississippi
Greenfield, Jack, National Tung Oil Marketing Cooperative, Inc., Whippany, N. J.
Murray, Charles A., Crosby Forest Products Co., Picayune, Mississippi
Nobles, W. L., University of Mississippi, University, Mississippi
Potter, George F., USDA, ARS, HC, Bogalusa, Louisiana
Rowlands, Lamont, Tung Growers Council of America, Picayune, Mississippi
Sanderson, John M., National Tung Oil Marketing Cooperative, Inc., Babylon, N. Y.
Shannon, George W., Farm Editor, WWL and Tung World, New Orleans, Louisiana
Nelb, R. G., Vibrin Development, U. S. Rubber Co., Naugatuck, Conn.

SURB Staff

Altschul, A. M.
Bickford, W. G.
Dollear, F. G.
Fisher, C. H.
Goheen, G. E.
Goldblatt, L. A.
Hoffman, Joan
Holmes, R. L.
Hopper, Lucien L., Jr.
McKinney, R. S.
Planck, R. W.
Rayner, E. T.
Kime, J. A.
Pollard, E. F.

United States Department of Agriculture
Agricultural Research Service
Southern Utilization Research Branch

Meeting, January 5, 1956 of

TUNG INDUSTRY INFORMAL RESEARCH COMMITTEE

Southern Regional Research Laboratory
New Orleans, Louisiana

10:00 A. M. Welcome - C. H. Fisher, Chief, SURB
Opening Remarks - R. C. Goodwin, Chairman, Presiding
Review of Tung Research at the Southern Utilization Research Branch
A. M. Altschul, Head, Oilseed Section, SRRL
L. A. Goldblatt, Supervisor, Oil Chemistry Unit
Polyester Resins -- What Can Tung Oil Contribute?
R. G. Nelb, Manager, Vibrin Development, U. S. Rubber Co.
Progress in the Promotion and Development of the Use of Tung Oil
John M. Sanderson, National Tung Oil Marketing Cooperative, Inc.
Jack Greenfield, National Tung Oil Marketing Cooperative, Inc.
Report on Tung Oil Specifications
L. A. Goldblatt

12:30 P. M. Lunch — Lobby, SRRL

1:00 P. M. Conference Room — Film, The Story of Tung
Courtesy, Crosby Forest Products Co.
Tour of Laboratories
Room 2110 Tung Oil Derivatives — W. G. Bickford & Joan Hoffman
Tung Oil Monoglycerides — R. S. McKinney
Room 2113 Tung Oil in Surface Coatings, L. L. Hopper, Jr., Fellow, National Tung Oil Marketing Coop., Inc.
The Ether-Soluble Toxin of Tung Kernels, R. L. Holmes

2:00 P. M. Conference Room
Status of the Tung Industry — Marshall Ballard, Jr. President, American Tung Oil Association
General Discussion of Present Program and Need for Additional Research

DIRECTORY OF PERTINENT U. S. D. A. PERSONNEL

Ezra T. Benson	Secretary, U. S. Department of Agriculture
Byron T. Shaw	Administrator, Agricultural Research Service
George Irving	Deputy Administrator for Research, Agricultural Research Service

Utilization Research

G. E. Hilbert	Director, Utilization Research
Walter M. Scott	Assistant Director, Utilization Research
J. R. Matchett	Assistant Director, Utilization Research
C. H. Fisher	Chief, Southern Utilization Research Branch
G. E. Goheen	Assistant Chief, SURB
J. A. Kime	Assistant to Chief, SURB
A. M. Altschul	Head, Oilseed Section, SURB
T. H. Hopper	Head, Analytical, Physical-Chemical and Physics Sec., SURB
E. A. Gastrock	Head, Engineering & Development Section, SURB
F. G. Dollear	Assistant Head, Oilseed Section, SURB
L. A. Goldblatt	Supervisor, Oil Chemistry Unit, Oilseed Section, SURB
R. W. Planck	Supervisor, Biochemistry Unit, Oilseed Section, SURB
R. S. McKinney	In Charge, U. S. Tung Oil Laboratory, Bogalusa, La.
W. G. Bickford	Chemist, Oil Chemistry Unit
R. L. Holmes	Chemist, U. S. Tung Oil Laboratory, Bogalusa, La.
Joan Hoffman	Chemist, Oil Chemistry Unit
E. T. Rayner	Chemist, U. S. Tung Oil Laboratory, Bogalusa, La.
L. L. Hopper, Jr.	Fellow, National Tung Oil Marketing Cooperative, Inc.

SOUTHERN REGIONAL RESEARCH LABORATORY

Tour of Tung Research January 5, 1956

TUNG OIL IN SURFACE COATINGS

Tung oil is a premium drying oil but its great reactivity makes it difficult to process by conventional procedures. The object of this work was to develop practical, useful cooking procedures for the production of premium vehicles for use in paints and varnishes. Another object was to take advantage of the great reactivity of tung oil to introduce essentially nondrying materials to decrease the reactivity but at the same time to impart additional desirable properties, for example, mildew resistance.

Two methods were developed to make safer the preparation of vehicles containing tung oil or tung oil fatty acids.

(1) The use of zinc resinate as the ester exchange agent and gel dispersing medium.

(2) Two phase cooking, i. e., cooking epoxy resins with some fatty acids in phase 1 and adding tung oil fatty acids in phase 2.

This work has aroused the active interest of chemists of the Shell Oil Company in developing formulations using their Epon resins and tung oil fatty acids.

Tung oil containing vehicles, which have been prepared using tripropionin to introduce "built in" meldew resistance, seem promising.

SOUTHERN REGIONAL RESEARCH LABORATORY

Tour of Tung Research January 5, 1956

THE ETHER-SOLUBLE TOXIN OF TUNG KERNELS

Tung meal is highly toxic to animals and so cannot be used as feed. It contains at least two toxic substances. One of these is insoluble in organic solvents and can be detoxified and rendered harmless by heating. The other substance is soluble in organic solvents and is not changed by moderate heating.

Research is being conducted on the isolation, characterization and identification of the second toxin. Finely powdered (hexane extracted) meal has been extracted with ether or other suitable solvent to remove the toxin in a crude form. Methods have been worked out for concentrating this material to give a highly toxic fraction. The final step in the process involves the use of a Craig counter-current extractor.

Pilot-plant methods have been developed for extracting larger batches of meals to give adequate quantities of concentrates for feeding tests and chemical study.

The original oil-free tung meal, the ether-extracted meal, and concentrates from the ether extracts have been tested on young chicks at the Poultry Industry Department, Louisiana State University. All of these samples were toxic, the most active being the concentrated ether extract.

Work is being continued with the ultimate aim of learning enough about the toxins to permit the development of a practical method for detoxifying the meal and for analyzing processed meals for the presence of toxin.

SOUTHERN REGIONAL RESEARCH LABORATORY

Tour of Tung Research January 5, 1956

TUNG OIL MONOGLYCERIDES

The monoglycerides of tung oil have potential value as emulsifiers, sticking agents, and plasticizers and in the preparation of alkyds and other surface finishes. The objective of this work is to develop practical methods of preparing tung oil monoglycerides, to determine their chemical and physical properties and to characterize pure glycerol monoeleostearate.

It was found that the usual methods for preparing monoglycerides by direct glycerolysis could not be used because of the highly reactive nature of tung oil fatty acids. A product containing about 75% monoglycerides of tung oil fatty acids has been obtained through the use of sodium methoxide (catalyst) and pyridine (solvent).

Analysis of the products for monoglyceride content proved quite difficult, as the usual methods for determining monoglycerides gave erratic and frequently obviously erroneous results. A reasonably satisfactory method for the determination of glycerol monoeleostearate was devised.

The addition of one, two and three percent tung oil monoglycerides to cottonseed oil lowered its interfacial tension to water by 58.5, 90.4, and 96.1%, respectively. The addition of 0.005 and 0.01 percent tung oil monoglycerides to water lowered its surface tension by 50.3 and 53.8%, respectively.

Crude tung oil monoglycerides (32.1%) heated to 572° F. bodied, but did not gel like tung oil; these bodied monoglycerides, after the addition of mineral spirits and lead and manganese driers, dried to a smooth film without wrinkling.

Tung oil monoglycerides have been fractionated using various solvents, but this method has proved unsatisfactory for obtaining pure glycerol monoeleostearate.

SOUTHERN REGIONAL RESEARCH LABORATORY

Tour of Tung Research January 5, 1956

TUNG OIL DERIVATIVES

Preparations of chemicals and intermediates from tung oil by the addition of special reagents to the unsaturated centers of tung oil acids are being made in an effort to extend the utilization of tung oil.

The following compounds have been reacted with α- and β-eleostearic acids and esters: β-propiolactone, acrylonitrile, fumaronitrile, maleic anhydride, chloromaleic anhydride, benzoquinone, and acrylamide.

These products are being screened for biological activity and as plasticizers.

Further information regarding the fundamental nature of the α- and β-eleostearic acids of tung oil is being sought through a kinetic study of their rates of reaction with certain reagents.

Simplified methods for the preparation of pure α-and β-eleostearic acids have been developed. Ultraviolet data obtained on these highly pure acids serve as a basis for the more accurate determination of the α- and β-eleostearic acid contents of tung oil. A manuscript, "The Reaction of β-Propiolactone with α- and β-Eleostearates and Plasticizer Properties of Derived Esters," has been published.

Another manuscript, "The Reaction of Acrylonitrile and Fumaronitrile with α- and β-Eleostearates, Plasticizer Properties of the n-Butyl Esters of the Adducts," is being submitted to the same journal.